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(54) TITLE OF THE INVENTION

Silicon nitride ceramic sintered compact

(57) ABSTRACT

PURPOSE

To provide a silicon nitride ceramic sintered compact excellent in high strength, high toughness, and thermal shock resistance.

CONSTITUTION

A silicon nitride ceramic sintered compact comprising 100 parts by weight of silicon nitride ceramic and between 2 and 25 parts by weight of titanium carbonitride solid solution with a TiC/TiN weight ratio of between 5/5 and 9/1.

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CLAIMS

What is claimed is:

1. A silicon nitride ceramic sintered compact comprising 100 parts by weight of silicon nitride ceramic and between 2 and 25 parts by weight of titanium carbonitride solid solution with a TiC/TiN weight ratio of between 5/5 and 9/1.

DETAILED DESCRIPTION OF THE INVENTION

FIELD OF THE INVENTION

The present invention relates to a silicon nitride ceramic sintered compact excellent in high hardness, high toughness, and thermal shock resistance.

DESCRIPTION OF THE RELATED ART

Silicon nitride ceramic has recently become used in metal wire rod rolling rolls and guide rolls, and have contributed to an increase in the life span of the rolls and the quality of the wire rods (Japanese Publication of Unexamined Patent Application S59-21413 (1984)). However, although there are no problems with the relatively moderate conditions of the cold rolling process and guide rolls, problems arise in the hot rolling process, which has more strenuous conditions, wherein cracks and surface roughness etc. generate due to thermal shocks.

Further, as an abrasion-resistant tool, although silicon nitride ceramic in which 1 or more carbide, nitride and carbonitride of Ti, Zr and Hf are selected to be included therein as a dispersion phase-forming constituent, which is used for its excellent abrasion resistance quality (Japanese Publication of Unexamined Patent Application S59-199579 (1984)), it is inferior in thermal shock resistance and hence cannot be used in regions where there are thermal shocks, and as a result silicon nitride's excellent qualities have not been used to their full potential.

The present inventors took such conditions into consideration and advanced research on silicon nitride ceramic sintered compacts that have high hardness and high toughness without any impairment to thermal shock resistance, and as a result discovered the beneficial results of including a titanium carbonitride solid solution with a specific TiC/TiN ratio therein, and thus completed the present invention.

PROBLEMS TO BE RESOLVED BY THE INVENTION

The present invention aims to provide a silicon nitride ceramic sintered compact excellent in high hardness, high toughness, and thermal shock resistance, which is suitable as an abrasion-resistant material in regions where thermal shocks are intense.

MEANS FOR SOLVING THE PROBLEMS

Namely, the present invention is a silicon nitride ceramic sintered compact comprising 100 parts by weight of silicon nitride ceramic and between 2 and 25 parts by weight of titanium carbonitride solid solution with a TiC/TiN weight ratio of between 5/5 and 9/1.

The present invention shall now be described in further detail.

The silicon nitride ceramic pertaining to the present invention consists of silicon nitride and a sintering agent. One or a combination of the following can be used as the sintering agent: MgO, Al₂O₃, Y₂O₃, CoAl₂O₄, MgAl₂O₄, and AlN. AlN is useful for crystallizing the grain boundary. The percentage of the sintering agent is typically between 3 and 20 parts by weight for every 100

parts by weight of silicon nitride.

It is preferable for a solid solution powder to be used as the titanium carbonitride dispersion phase-forming constituent. If a powder mixture of a carbide and nitride of titanium is used, a solid solution cannot be sufficiently formed in the sintered compact and thermal shock resistance is inferior, which is undesirable. It is preferable for the weight ratio of TiC/TiN in the titanium carbonitride solid solution to be between 5/5 and 9/1, and particularly preferable for it to be between 6/4 and 8/2. If the TiC/TiN weight ratio is smaller than 5/5, hardness decreases, which is undesirable. If it is larger than 9/1, thermal shock resistance markedly deteriorates, which is also undesirable. The existence of a titanium carbonitride solid solution can be confirmed by means of EPMA etc.

It is preferable for between 2 and 25 parts by weight, and particularly preferable for between 5 and 20 parts by weight, of the titanium carbonitride dispersion phase-forming constituent to be included for every 100 parts by weight of silicon nitride ceramic. If less than 2 parts by weight are included, the abrasion resistance of the sintered compact is inferior. If more than 20 parts by weight are included, thermal shock resistance is inferior.

Although the silicon nitride ceramic sintered compact according to the present invention can be suitably used in metal wire rod rolling rolls and guide rolls, it can also be used as an abrasion-resistant material in welding jigs, cutting tools, etc.

The silicon nitride ceramic sintered compact according to the present invention can be manufactured by means of the following methods. Namely, 5 to 10 parts by weight of a sintering agent are added to 90 to 95 parts by weight of Si₃N₄ powder with an average particle diameter of between 0.8 and 1.0 μm to obtain 100 parts by weight of a silicon nitride ceramic raw powder. Next, between 2 and 25 parts by weight of a titanium carbonitride solid solution powder with an average particle diameter of 4 μm or less and a prescribed TiC/TiN weight ratio is added to the silicon nitride ceramic raw powder for every 100 parts by weight and turned into a mixed raw powder. This mixed raw powder can then be manufactured into the silicon nitride ceramic sintered compact according to the present invention by means of firing it. If the average particle diameter of the Si₃N₄ is larger than 1.0 μm, toughness and hardness both decrease. Conversely, if the average particle diameter of the titanium carbonitride powder is larger than 4 μm, thermal shock resistance tends to become inferior.

The prescribed amounts of each of the raw materials in the mixed raw powder described above can be adjusted by means of wet blending them in a pole mill with an organic solvent such as trichloroethane for 1-5 hours, drying it, then pulverizing it. The mixed powder is then press formed and fired by means of the cold isostatic press method (CIP method), followed by the pressureless sintering method. The hot press method or hot isostatic press method (HIP method) may also be employed, depending on the form and required qualities.

In the event that the hot press method is employed, the mixed raw powder described above is loaded into a graphite die and preliminarily compressed therein at 100 Kg/cm². It is then sintered at a temperature between 1600 and 1800°C at a pressure of between 100 and 400 Kg/cm². In the event that the HIP method is employed, the mixed raw powder described above is formed into a compact with a relative density of 50% or higher by means of the cold isostatic press method (CIP method) at a pressure between 1000 and 3000 Kg/cm². The compact is then preliminarily sintered at a typical sintering temperature between 1600 and 1800°C to create a sintered compact with a relative density of 95% or higher. The sintered compact is then further sintered in a nitrogen atmosphere with a pressure between 500 and 2000 atm at a temperature between 1500 and 1800°C.

WORKING EXAMPLES

The present invention shall now be described in detail by way of working examples and comparative examples.

Working Examples 1-5 and Comparative Examples 1-6

A titanium carbide or titanium carbonitride solid solution (commercially available; 1.4 μ m average particle diameter grade) was added in the percentages shown in Table 1 to a mixed powder with 100 parts by weight, consisting of 93 parts by weight of Si_3N_4 with an average particle diameter of 1 μ m, 1.6 parts by weight of MgO , 1 part by weight of Al_2O_3 , 2.4 parts by weight of Y_2O_3 , and 2 parts by weight of AlN . Wet blending was then carried out for 1 hour using trichloroethane as the solvent, and the mixed raw powder was adjusted. The mixture was then hot press sintered at a pressure of 160Kg/cm² and a temperature of 1750°C. A test piece was cut off of

the obtained sintered compact and was measured for hardness, fracture toughness value, thermal shock resistance (thermal shock temperature) and abrasion resistance (abrasion volume). The results are shown in Table 1. These properties were measured by means of the following methods.

(1) Hardness: Vickers 20Kg load

(2) Fracture toughness value: The IM method

(3) Thermal shock resistance: Cut off a test piece from the sintered compact with dimensions of 3×4×40mm in conformity with JIS 1601 and placed it in a siliconit electric furnace at a prescribed temperature, after which it was immersed in water and measured for flexural strength. The temperature immediately prior to the decrease in strength was made the thermal shock resistance temperature.

(4) Abrasion resistance: The ring-on-disc method. A copper ring was intruded under water at 125Kg/cm², then rotated at a circumferential velocity of 0.1m/s for 1 hour. The abrasion volume was then examined.

Table 1

	Added amount of titanium carbonitride (parts by weight)	Weight ratio of TiC/TiN	Properties of sintered compact			
			Hardness (Hv)	Fracture toughness value (Mpa·m ^{1/2})	Thermal shock resistance temperature (°C)	Abrasion volume (×10 ⁻³ cm ³)
Working example 1	15	8/2	1600	10.0	700	2.0
Working example 2	15	6/4	1550	9.2	700	2.0
Working example 3	15	5/5	1550	9.1	700	2.0
Working example 4	5	6/4	1550	9.0	700	2.5
Working example 5	20	6/4	1550	10.2	700	2.0
Comparative example 1	0	-	1530	7.7	700	3.5
Comparative example 2	10	10/0	1560	7.4	700	3.0
Comparative example 3	15	10/0	1580	8.5	500	2.0
Comparative example 4	15	3/7	1430	9.2	700	2.5
Comparative example 5	30	6/4	1550	9.4	500	1.8
Comparative example 6	TiC 7.5 TiN 7.5	* 5/5	1590	8.0	500	2.0

* indicates a mixed powder rather than a solid solution

As is made clear in Table 1, the silicon nitride ceramic sintered compact according to the present invention has good abrasion resistance, has high hardness and high toughness, and is excellent in thermal shock resistance.

EFFECT OF THE INVENTION

The silicon nitride ceramic sintered compact with titanium carbonitride solid solution dispersed therethroughout according to the present invention is excellent in high hardness, high toughness, and thermal shock resistance. Consequently, it is suitable for metal wire rod rolling rolls and guide rolls that require high hardness and high toughness for the frequent addition of thermal shocks, and can also be used as an abrasion-resistant material in welding jigs, cutting tools, etc.

(9)

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(54) SILICON NITRIDE CERAMIC SINTERED BODY

(57)Abstract:

PURPOSE: To obtain a silicon nitride ceramic sintered body excellent in hardness, toughness, thermal shock resistance, etc., and suitable for reduction rolls for metal by compounding a specified amt. of titanium carbide nitride solid soln. powder of a specified compsn. to a powder of silicon nitride ceramic source material and then calcining the mixture.

CONSTITUTION: (A) 100 pts.wt. of powder of the silicon nitride ceramic source material and (B) 2-25 pts.wt. of titanium carbide nitride solid soln. powder are mixed. The powder (B) has 5/5 to 9/1 weight ratio of TiC/TiN. Then the mixture powder is molded by press molding, etc., and calcined by a hot press method, etc., to produce the objective silicon nitride ceramic sintered body. By this method, the titanium carbide nitride solid soln. can be incorporated as a dispersion phase component into the silicon nitride ceramic, so that hardness, toughness, etc., of the sintered body can be improved without decreasing the thermal shock resistance. As for the sintering aid added to the component (A), AlN, Y₂O₃, etc., are preferable.

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(54) 【発明の名称】 窒化珪素質セラミック焼結体

(57) 【要約】

【目的】 高強度、高韧性且つ耐熱衝撃性に優れた窒化珪素質セラミック焼結体の提供。

【構成】 窒化珪素質セラミック 100 重量部に対し、TiC/TiN 重量比が 5 / 5 ~ 9 / 1 の範囲にあるチタン炭窒化物固溶体 2 ~ 25 重量部を含有してなることを特徴とする窒化珪素質セラミック焼結体。

【特許請求の範囲】

【請求項 1】 窒化珪素質セラミック 100 重量部に対し、 TiC / TiN 重量比が $5/5 \sim 9/1$ の範囲にあるチタン炭窒化物固溶体 2~25 重量部を含有してなることを特徴とする窒化珪素質セラミック焼結体。

【発明の詳細な説明】

【0001】

【産業上の利用分野】 本発明は、高硬度、高靱性且つ耐熱衝撃性に優れた窒化珪素質セラミック焼結体に関する。

【0002】

【従来の技術】 近年、金属線材圧延ロール及びガイドロールに窒化珪素質セラミックが利用されるようになり、ロールの寿命と線材の品質の向上に寄与してきた（特開昭 59-21413 号公報）。しかし、冷間圧延工程やガイドロール等の比較的条件の緩やかな所では問題はないが、条件のより厳しい熱間圧延工程では、ヒートショックによる割れや表面の肌荒れ等が発生し問題であった。

【0003】 また、耐摩耗工具として、窒化珪素質セラミックに、分散相形成成分として Ti 、 Zr 、 Hf の炭化物、窒化物及び炭窒化物から選ばれた 1 種又は 2 種以上含有させた耐摩耗性に優れたセラミックが利用されているが（特開昭 59-199579 号公報）、耐熱衝撃性に劣るのでヒートショックの加わる部位には使用できず、窒化珪素の優れた特性が活かされてはいなかった。

【0004】 本発明者らは、このような状況に鑑み、耐熱衝撃性を損なうことなく、高硬度、高靱性を有する窒化珪素質セラミック焼結体について研究を進めた結果、特定の TiC / TiN 比のチタン炭窒化物固溶体を含有せしめればよいことを見出し、本発明を完成したものである。

【0005】

【発明が解決しようとする課題】 本発明の目的は、高硬度、高靱性且つ耐熱衝撃性に優れ、熱衝撃の激しい部位の耐摩耗材として好適な窒化珪素質セラミック焼結体を提供することにある。

【0006】

【課題を解決するための手段】 すなわち、本発明は、窒化珪素質セラミック 100 重量部に対し、 TiC / TiN 重量比が $5/5 \sim 9/1$ の範囲にあるチタン炭窒化物固溶体 2~25 重量部を含有してなることを特徴とする窒化珪素質セラミック焼結体である。

【0007】 以下、本発明について詳細に説明する。

【0008】 本発明に係る窒化珪素質セラミックは、窒化珪素と焼結助剤とで構成されており、その焼結助剤としては、 MgO 、 Al_2O_3 、 Y_2O_3 、 CoAl_2O_4 、 MgAl_2O_4 、 AlN 等を単独あるいは組み合わせで用いることができる。 AlN は粒界を結晶化させるために有用である。焼結助剤の割合は、通常、窒化珪素 100 重量部に対し 3~20 重量部である。

【0009】 分散相形成成分のチタン炭窒化物としては固溶体粉末を用いたほうが好ましい。チタンの炭化物、窒化物の混合粉末を用いると、焼結体中で十分に固溶体を形成せず、耐熱衝撃性が劣り好ましくない。チタン炭窒化物固溶体の TiC / TiN 重量比は $5/5 \sim 9/1$ であることが好ましく、さらに好ましくは $6/4 \sim 8/2$ である。 TiC / TiN 重量比が $5/5$ より小さいと硬度が低下し、また $9/1$ より大きいと耐熱衝撃性が著しく劣化するので好ましくない。チタン炭窒化物固溶体の存在は E P M A 等により確認することができる。

【0010】 分散相形成成分のチタン炭窒化物固溶体は、窒化珪素質セラミック 100 重量部に対し、2~25 重量部、特に 5~20 重量部を含有させることが好ましい。2 重量部未満では焼結体の耐摩耗性が劣り、20 重量部を越えると耐熱衝撃性が劣る。

【0011】 本発明の窒化珪素質セラミック焼結体の用途としては、金属圧延ロール、ガイドロールが好適であるが、溶接治具や切削工具等の耐摩耗部材としても使用できる。

【0012】 本発明の窒化珪素質セラミック焼結体は以下の方法によって製造することができる。すなわち、平均粒径 $0.8 \sim 1.0 \mu\text{m}$ 程度の Si_3N_4 粉末 90~95 重量部に焼結助剤 5~10 重量部を加えて窒化珪素質セラミック原料粉末 100 重量部を得る。次に平均粒径 $4 \mu\text{m}$ 以下の所定 TiC / TiN 重量比のチタン炭窒化物固溶体粉末を窒化珪素質セラミック原料粉末 100 重量部に対し 2~25 重量部加えて混合原料粉末となし、それを焼成することによって本発明の窒化珪素質セラミック焼結体を製造することができる。 Si_3N_4 粉末の平均粒径が $1.0 \mu\text{m}$ より大きいと靱性、硬度共に低下し、一方、チタン炭窒化物粉末の平均粒径が $4 \mu\text{m}$ より大きいと耐熱衝撃性が劣る傾向がある。

【0013】 上記混合原料粉末は、それぞれの原料の所定量を、クロロセン等の有機溶媒と共にボールミルにて 1~5 時間の湿式混合を行い、乾燥後、解砕することによって調整することができる。混合粉末はプレス成形、冷間静水圧法（CIP 法）後常圧焼結法で焼成する。形状や要求特性により、ホットプレス法、熱間静水圧法（HIP 法）を採用することもできる。

【0014】 ホットプレス法の場合には、上記混合原料粉末を黒鉛ダイスに充填し、 $100\text{Kg}/\text{cm}^2$ 程度に予備圧縮した後、温度 $1600 \sim 1800^\circ\text{C}$ 、圧力 $100 \sim 400\text{Kg}/\text{cm}^2$ で焼結する。また、HIP 法を利用する場合は、上記混合原料粉末を $1000 \sim 3000\text{Kg}/\text{cm}^2$ の圧力で冷間静水圧法（CIP 法）によって相対密度 50% 以上の成形体となし、次いで予備焼結として温度 $1600 \sim 1800^\circ\text{C}$ の常圧焼結を行って相対密度 95% 以上の焼結体を作製し、さらにその焼結体を温度 $1500 \sim 1800^\circ\text{C}$ 、圧力 $500 \sim 2000\text{atm}$ の窒素雰囲気下で HIP 焼結を行う。

【0015】

【実施例】以下、実施例と比較例をあげてさらに具体的に本発明を説明する。

【0016】実施例1～5 比較例1～6

平均粒径1 μm の Si_3N_4 粉末93重量部と焼結助剤 MgO 1.6重量部、 Al_2O_3 1重量部、 Y_2O_3 2.4重量部、 AlN 2重量部とからなる混合粉末100重量部に対し、Tiの炭化物又は炭窒化物固溶体（市販品：平均粒径1.4 μm グレード）を表1に示す割合で添加し、クロロセンを溶媒として1時間の湿式混合を行い混合原料粉末を調整した。これを温度1750℃、圧力160Kg/cm² でホットプレス焼結した。得られた焼結体よりテストピースを切り出し、硬度、破壊靱性値、耐熱衝撃性（耐熱衝撃温度）及び耐摩耗性（摩耗体積）を測定した。それらの結果を表1に示す。

【0017】物性は以下の方法により測定した。

（1）硬度：ピッカース 20Kg 荷重により測定した。

（2）破壊靱性値：IM法により測定した。

（3）耐熱衝撃性：焼結体より JIS 1601 に準拠した3×4×40mmのテストピースを切り出し、シリコニット電気炉で所定温度に保持した後、水中に落下させ、曲げ強度を測定し、強度低下の起こる直前の温度を測定し耐熱衝撃温度とした。

（4）耐摩耗性：リングオンディスク法で評価した。水中で銅リングを125Kg/cm² で押し付け、周速0.1m/sで1hrリングを回し、摩耗体積を求めた。

【0018】

【表1】

表 1

	Ti炭窒化物 添加量 (重量部)	TiC/TiN 重量比	焼 結 体 物 性			
			硬度 (Hv)	破壊靱性値 MPa·m ^{1/2}	耐熱衝撃温度 (℃)	摩耗体積 (×10 ⁻³ cm ³)
実施例1	15	8/2	1600	10.0	700	2.0
実施例2	15	6/4	1550	9.2	700	2.0
実施例3	15	5/5	1550	9.1	700	2.0
実施例4	5	6/4	1550	9.0	700	2.5
実施例5	20	6/4	1550	10.2	700	2.0
比較例1	0	—	1530	7.7	700	3.5
比較例2	10	10/0	1560	7.4	700	3.0
比較例3	15	10/0	1580	8.5	500	2.0
比較例4	15	3/7	1430	9.2	700	2.5
比較例5	30	6/4	1550	9.4	500	1.8
比較例6	TiC 7.5 TiN 7.5	* 5/5	1590	8.0	500	2.0

*固溶体でなく混合粉末

靱性であり、しかも耐熱衝撃性に優れていることがわかる。

【 0 0 2 0 】

【発明の効果】本発明のチタン炭窒化物固溶体分散の窒化珪素質セラミック焼結体は、高硬度、高靱性且つ耐熱

衝撃性に優れたものである。従って、熱衝撃が頻繁に加わり高硬度、高靱性を必要とする金属圧延ロールやガイドロールに好適であるが、溶接治具、切削工具等の耐摩耗部材としても使用することができる。

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